ARKIV FÖR FYSIK Band 13 nr 39

Communicated 22 January 1958 by ERIK HULTHÉN and OSKAR KLEIN

Theoretical determination of the electronic polarizability of lithium, calcium and scandium

By MARIANNE SUNDBOM

With 1 figure in the text

SUMMARY

The electronic polarizability α has been determined by perturbation methods for Li, Ca^{++}, Ca and Sc. The numerical calculations have been performed on the Swedish electronic digital computor BESK. The calculated values of α (α in units 10^{-24} cm^3) are: 20 for Li, 0.83 for Ca^{++}, 52–153 for Ca and 154 for Sc. Although these values of α probably are not very exact, they are however certainly of the correct order of magnitude.

Introduction

A great many experimental investigations have been performed to determine the electronic polarizability α of ions [1]. In most cases, α has been determined for ions with rare-gas-like configurations. However, Drechsler, Müller and Henkel [2], [3] have worked out a method for measuring α of other species with the field emission microscope. They have published experimental values of α for Li, Ba, [2] and some metallic atoms [4].

Kirkwood's variation method has been used several times for theoretical determinations of α. This is the case with works by e.g. Buckingham [5] and Guy and Harrand [6]. Pople and Schofield [7] have recently improved the method and applied it to argon. Moreover perturbation methods have been used by Sternheimer [1], [8], who has calculated α for atoms with rare-gas-like configurations, i.e. s^2p^6 and $s^2p^6d^{10}$.

In a preliminary report [9] we have pointed out that it would be of great interest to find even rather approximate values for the electronic polarizability α of atoms and ions with partly filled d-shells. Therefore an attempt was made to find the order of magnitude of this polarizability from a simple perturbation calculation. Atoms with one, two or three electrons outside the rare-gas-like configurations were considered and the result was applied to lithium $1s^2 2s$, calcium $4s^2$ and scandium $3d4s^2$.

Theory

The Hamiltonian of an atom in a uniform field E is[1]

$$H = H_0 + E \sum_i r_i \cos \vartheta_i \tag{1}$$

---

[1] Atomic units are used in the formulae throughout the paper.

where r_i and ϑ_i are spherical polar coordinates of the i^{th} electron. The polar axis has the direction of the electric field. H_0 is the Hamiltonian of the free atom.

When treating the effect of the electric field, it is first necessary to decide how the order of magnitude for the perturbing potential, $E\sum_i r_i \cos\vartheta_i$, compares with the other terms in the Hamiltonian [10]. Here the case is considered where the effect of the electric field is large compared with the spin-orbit interactions but small compared with the Coulomb interactions. As unperturbed Hamiltonian we then have:

$$H_0 = \sum_i \left(-\tfrac{1}{2}\Delta_i - \frac{Z}{r_i} \right) + \sum_{j<i} \frac{1}{r_{ij}} \tag{2}$$

With this Hamiltonian the energy levels are classified by terms represented by the symbol ${}^{2S+1}L$. In the presence of the uniform field E we have axial symmetry and each term ${}^{2S+1}L$ splits up, so that states with different $|M_L|$ have different energy values. In the case of scandium, the ground state is $3d\,4s^2\,{}^2D$. The M_L values are directly given by the m_l values of the $3d$-electron: $(m_l = 0, \pm 1, \pm 2)$. The wave function for a special value of M_L can thus be written as a single Slater determinant of unperturbed one-electron wave functions, $\varphi_i(\boldsymbol{r}_t, \zeta_t)$, where $\boldsymbol{r}_t$ is the space coordinate and ζ_t is the spin coordinate of the t^{th} electron. We can thus consider our problem as a perturbed Hartree-Fock problem.

The problem is now to determine the first-order perturbation φ_i' of the functions φ_i. The energy can be determined up to the second order from φ_i and φ_i'. It can be shown [11] that the first and second order perturbation energies take the form:

$$\mathcal{E}_1 = \sum_i \int \varphi_i^* E\, r \cos\vartheta\, \varphi_i\, d\tau = 0 \tag{3}$$

$$\mathcal{E}_2 = \sum_i \int \varphi_i^* E\, r \cos\vartheta\, \varphi_i'\, d\tau \tag{4}$$

where φ_i' is given by the equation:

$$\begin{aligned} &\left(-\tfrac{1}{2}\Delta_2 - \frac{Z}{r_2} - \varepsilon_i \right) \varphi_i'(2) + \sum_i [(j|q|j\,i') - (j|q|i'j)] = \\ &= -E\,r_2 \cos\vartheta_2\, \varphi_i(2) - \sum_j [(j'|q|j\,i) + (j|q|j'i) - (j'|q|i\,j) - (j|q|i\,j')] + \varepsilon_i'\, \varphi_i(2) \end{aligned} \tag{5}$$

In (5) $(j'|q|j\,i) = \int \varphi_j'^*(1) \dfrac{1}{r_{12}} \varphi_j(1)\, \varphi_i(2)\, d\tau_1$ etc.

ε_i is the orbital energy. By multiplying equation (5) by φ_i^* and integrating, ε_i' is given by:

$$\varepsilon_i' = \sum_j [(j'i|q|j\,i) + (j\,i|q|j'i) - (j'i|q|i\,j) - (j\,i|q|i\,j')] \tag{6}$$

where $(j'i|q|j\,i) = \int \varphi_j'^*(1)\, \varphi_i^*(2) \dfrac{1}{r_{12}} \varphi_j(1)\, \varphi_i(2)\, d\tau_1\, d\tau_2$ etc.

The fact that $\mathcal{E}_1 = 0$ is equivalent to the fact that the atom has no permanent electric dipole moment [12]. As is well known, the electronic polarizability α is defined by the equation

$$\mathcal{E}_2 = -\tfrac{1}{2}\alpha E^2 \tag{7}$$

The induced electric dipole moment is αE.

The purpose of this investigation was to find the order of magnitude of α. As it would be very laborious to work with the equations (5), the author has used an approximation of (5), namely:

$$(-\tfrac{1}{2}\Delta + V_0 - \varepsilon_i)\varphi_i' = -E r \cos\vartheta\,\varphi_i \tag{8}$$

where

$$(-\tfrac{1}{2}\Delta + V_0 - \varepsilon_i)\varphi_i = 0 \tag{9}$$

For given functions φ_i, V_0 is given by (9). In (8), both the sum and the last term on the right hand side of (5) are neglected, i.e. the influence on the perturbation of φ_i from the perturbations of the other orbitals is neglected. This approximation will be discussed further in connection with the discussion of the results.

In the Hartree-Fock approximation the functions φ_i are of the form:

$$\varphi_i = \varphi_{nlm} = \frac{P_{nl}(r)}{r} Y_l^m(\vartheta,\varphi) f(\zeta). \tag{10}$$

From equation (8) and from the properties of $Y_l^m(\vartheta,\varphi)$ [13] it is seen that φ_i' will be of the form

$$\varphi_i' = (R_{l+1}(r) Y_{l+1}^m(\vartheta,\varphi) + R_{l-1}(r) Y_{l-1}^m(\vartheta,\varphi)) f(\zeta). \tag{11}$$

$R_{l+1}(r)$ and $R_{l-1}(r)$ can be written:

$$R_{l+1}(r) = -\frac{1}{r} P'_{l\to l+1}(r) 2E \sqrt{\frac{(l+1-m)(l+1+m)}{(2l+1)(2l+3)}}; \tag{12}$$

$$R_{l-1}(r) = -\frac{1}{r} P'_{l\to l-1}(r) 2E \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}}, \tag{13}$$

where $P'_{l\to l+1}$ and $P'_{l\to l-1}$ are given by the equations

$$\left[-\frac{d^2}{dr^2} + \frac{(l+1)(l+2)}{r^2} + 2V_0 - 2\varepsilon_i\right] P'_{l\to l+1} = r P_{nl}; \tag{14}$$

$$\left[-\frac{d^2}{dr^2} + \frac{(l-1)l}{r^2} + 2V_0 - 2\varepsilon_i\right] P'_{l\to l-1} = r P_{nl}, \tag{15}$$

as has been shown by Sternheimer [1].

In the case of the scandium atom one must determine which of the $|m|$-values assigned to the $3d$-orbital gives the lowest energy level. The contribution to $\mathcal{E}_2$ from $3d$ for different $|m|$ is:

$\|m\|$	$\mathcal{E}_2(3d)$
0	$-E^2\left(\frac{18}{35}\beta+\frac{8}{15}\gamma\right)$
1	$-E^2\left(\frac{16}{35}\beta+\frac{6}{15}\gamma\right)$
2	$-E^2\left(\frac{10}{35}\beta+0\right)$

where

$$\beta=\int_0^\infty P'_{3d\to f}\, r\, P_{3d}\, dr \tag{16}$$

and

$$\gamma=\int_0^\infty P'_{3d\to p}\, r\, P_{3d}\, dr \tag{17}$$

Now the calculation shows that β and γ are both positive. This means that $|m|=0$ gives the lowest energy level.

Numerical calculation

The equations (14) and (15) have been solved by numerical methods using the Swedish electronic digital computer BESK. (For further details, see appendix.) As far as the author knows, there are no exact determinations of the ground state orbitals for Sc. As unperturbed one-electron orbitals, the author therefore has simply used orbitals of the analytic form $r^n e^{-\mu r}$, obtained from Slater's rules. Thus the BESK-programme has been constructed for such orbitals. It is, however, easy to modify the programme so that orbitals which are numerically given can be used. Although numerical SCF-orbitals are available in the case of Li [14], Ca^{++} [15] and Ca [15], orbitals of the above-mentioned form have been used here also in these cases. The value of μ was, however, obtained by fitting the analytical orbital to the numerical one. In most cases, the exponent n was chosen to be an integer for computational reasons. In the case of the $4s$-orbital of Ca, n was also chosen equal to the Slater-rule n.

As a check on the programme the polarizability of Ca^{++}, previously calculated by Sternheimer [1], was computed. As is seen from Table 2, the agreement is satisfactory.

The computed value of α can be expected to depend strongly on the choice of the unperturbed functions φ_i [16] [17]. For an estimation of this dependence the polarizability α of Ca $4s^2$ was calculated for orbitals from Slater's rules and for analytical orbitals chosen to fit the best SCF-orbitals. In Table 1, those values of μ and n for Li, Ca^{++} and Ca, which are chosen to fit the best SCF-orbitals, are given.

Results

Results for the polarizabilities of Li, Ca^{++}, Ca and Sc are given in Table 2. It is seen that α of Ca and α of Sc are both much larger than α of Ca^{++}.

In Table 3, the contributions to α from the various shells are given for Li

Table 1. Values of μ and n for Li, Ca^{++} and Ca. μ chosen to fit the best SCF-orbitals.

Atom	Li		Ca^{++}		Ca	
Orbital	μ	n	μ	n	μ	n
$1s$	2.478	1				
$2s$	0.667	2				
$2p$	—	—				
$3s$	—	—	3.00	3	3.00	3
$3p$	—	—	2.83	3	2.83	3
$4s$	—	—	—	—	1.08	4
$4s$	—	—	—	—	0.987	3.7

Table 2. Calculated and experimental values of the electronic polarizability α.

Atom	α (10^{-24} cm^3)	Method	Author
Li	16 ± 3 20	experimental theor., μ chosen to fit the best SCF orb.	Drechsler and Müller [2] Present investigation
Ca^{++}	0.47–1.1 0.73 0.83	experimental theor., SCF orb. theor., μ chosen to fit the best SCF orb.	Tessmann, see [1] Sternheimer [1] Present investigation
Ca	153 52 57	theor., μ from Slater's rules theor., μ chosen to fit SCF orb. „	Present investigation „ „
Sc	154*	theor., μ from Slater's rules	Present investigation

* By mistake, incorrect figures were given for the values of α for Ca (Slater) and Sc in the preliminary report [9].

Table 3. The contribution to α from the various shells. α in 10^{-24} cm^3.

Atom / $(n\,l)$	Li	Sc
$(1s)$	0.03	10^{-5}
$(2s)$	20	0.002
$(2p)$	—	0.003
$(3s)$	—	0.24
$(3p)$	—	0.28
$(3d)$	—	26
$(4s)$	—	127

Table 4. The contribution to α of Ca from the $4s$ shell for three different choices of the unperturbed $4s$-orbital. α in 10^{-24} cm^3.

Orbital	Ca		
	$n(4s)$	$\mu(4s)$	$\alpha(4s)$
Slater's rule	3.7	0.77	152
Approx. of SCF . . .	4	1.08	51
Approx. of SCF . . .	3.7	0.987	56

and Sc. In the case of Li the contribution to α from the inner shell is negligible. In the case of Sc the same is true, i.e. the main contribution originates from $3d$ and $4s^2$.

Table 4 shows the contribution to α of Ca from the $4s$ shell for different choices of the unperturbed $4s$-orbital.

Discussion

From Table 2 it is seen that the author's calculated value for α of Ca^{++} lies within the range of the observed values. The value is slightly higher than Sternheimer's. The difference may be due to the fact that he used tabulated Hartree-Fock functions instead of which the present author used an analytical approximation. On the other hand, Sternheimer estimates the error in the values of α due to the interpolation procedure used to obtain φ_i' to be less than $\pm 20\,\%$, whereas the present author estimates this error to be less than $\pm 1\,\%$ (see appendix). The result for Ca^{++} shows that the BESK-programme functions satisfactorily.

From the results for Ca (Table 4) it is seen that the computed value of α is very sensitive to the choice of the unperturbed atomic orbitals. The value of α for the Slater's rule orbital differs by a factor of 3 from the values for the two orbitals chosen to fit SCF-orbitals.

It is difficult to estimate a numerical value for the error due to the fact that the approximate equation (8) has been used instead of the equation (5), but a rough estimate shows that this approximation would cause about the same percentage error in α for all calculated cases. Now the calculated values of α for Ca^{++} and Li are in good agreement with the experimental values, which could justify the approximation made.

The result of this investigation supports the assumption that the polarizabilities of calcium and scandium are considerably larger than the polarizabilities of closed shell atoms (for which detailed theoretical investigations already exist).

It is interesting to compare the polarizabilities of the s-electrons of different atoms. Some values are given in Table 5. It is seen that α increases with n and decreases with increasing charge within a certain period. It seems, however, as if the polarizability of H is unique, being much smaller than that for other atoms with valence electrons.

Table 5. Polarizabilities of one $n\,s$-electron.

Electron	Atom	α	
		Slater orb.	SCF orb.
$1\,s$	H	—	0.667
$2\,s$	Li	—	20
$4\,s$	Ca	76	26
$4\,s$	Sc	64	—

APPENDIX

Numerical methods used to solve the equations (14) and (15) on BESK

The Runge-Kutta method with constant intervals δ was used. The equations were integrated inward, starting at a large radius R with a value $P'(R)$. (Here the index of $P'_{l\to l\pm1}$ is omitted for convenience.) Integrations were carried out with different starting values $P'(R)$. The correct starting value $P'(R)$ is that for which the resulting $P'(r)$ is zero at $r=0$.

The following method was developed for the choice of $P'(R)$:

The first integration is carried out with a rough estimate of $P'(R)=P'_0(R)$, which value is to be given as a BESK parameter. The resulting function is denoted $P'_0(r)$ with the value $P'_0(0)$ at $r=0$. The following flow-diagram will show how the different values of $P'(R)$ are then automatically chosen.

The procedure is continued until we get a function $P'_n(r)$ for which $P'_n(0)/P'_{n\,\max}$ is less than a certain number and until $P'_{n+1}(r)$ and $P'_n(r)$ are sufficiently close and have different signs for $r=0$. In Table 6, the method is demonstrated for the actual case, $(2\,s\to p)$ for Li.

Table 6. Choice of $P'(R)$ for the actual case, $(2\,s\to p)$ for Li.

no.	$P'(R)$	sign of $P'(0)$
0	P'_0	−
1	$P'_0+\Delta$	−
2	$P'_0+2\,\Delta$	−
3	$P'_0+3\,\Delta$	−
4	$P'_0+4\,\Delta$	+
5	$P'_0+4\,\Delta-\frac{1}{2}\,\Delta$	−
6	$P'_0+4\,\Delta-\frac{1}{2}\,\Delta+\frac{1}{4}\,\Delta$	−
7	$P'_0+4\,\Delta-\frac{1}{2}\,\Delta+\frac{1}{4}\,\Delta+\frac{1}{8}\,\Delta$	+
8	$P'_0+4\,\Delta-\frac{1}{2}\,\Delta+\frac{1}{4}\,\Delta+\frac{1}{8}\,\Delta-\frac{1}{16}\,\Delta$	−

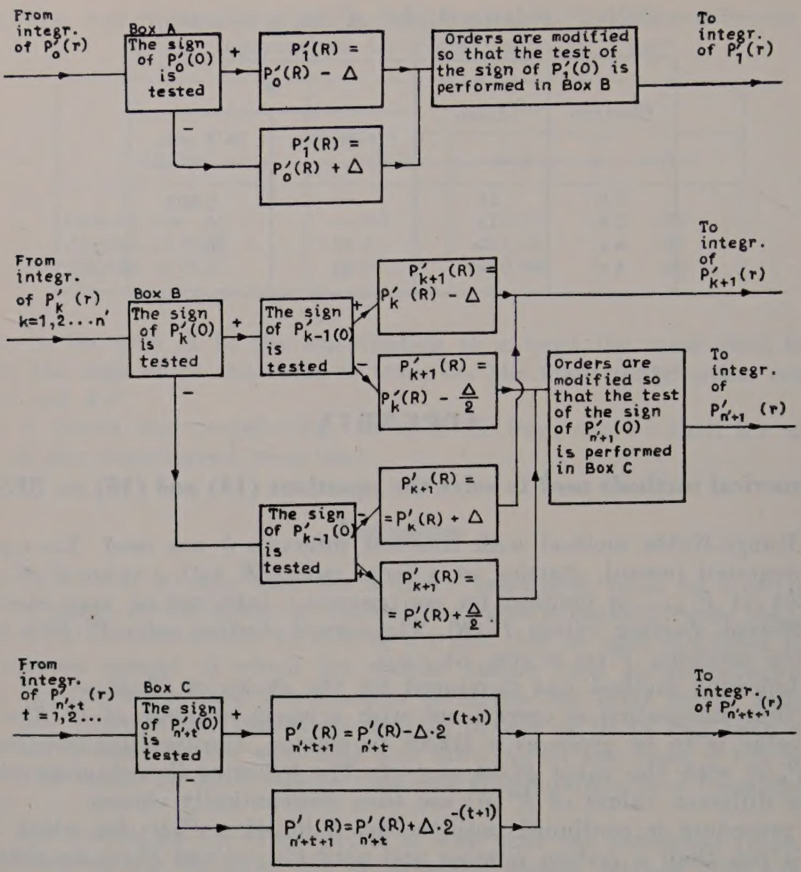
From integr. of $P'_0(r)$
Box A
The sign of $P'_0(0)$ is tested
+
$P'_1(R) = P'_0(R) - \Delta$
−
$P'_1(R) = P'_0(R) + \Delta$
Orders are modified so that the test of the sign of $P'_1(0)$ is performed in Box B
To integr. of $P'_1(r)$
From integr. of $P'_k(r)$ $k=1,2\ldots n'$
Box B
The sign of $P'_k(0)$ is tested
+
The sign of $P'_{k-1}(0)$ is tested
+
$P'_{k+1}(R) = P'_k(R) - \Delta$
−
$P'_{k+1}(R) = P'_k(R) - \frac{\Delta}{2}$
To integr. of $P'_{k+1}(r)$
Orders are modified so that the test of the sign of $P'_{n'+1}(0)$ is performed in Box C
To integr. of $P'_{n'+1}(r)$
−
The sign of $P'_{k-1}(0)$ is tested
−
$P'_{k+1}(R) = P'_k(R) + \Delta$
+
$P'_{k+1}(R) = P'_k(R) + \frac{\Delta}{2}$
From integr. of $P'_{n'+t}(r)$ $t=1,2\ldots$
Box C
The sign of $P'_{n'+t}(0)$ is tested
+
$P'_{n'+t+1}(R) = P'_{n'+t}(R) - \Delta \cdot 2^{-(t+1)}$
−
$P'_{n'+t+1}(R) = P'_{n'+t}(R) + \Delta \cdot 2^{-(t+1)}$
To integr. of $P'_{n'+t+1}(r)$

Fig. 1. Flow-diagram showing how the different values for $P'(R)$ are automatically chosen. Δ is to be given as a BESK parameter. Δ is positive for the equations (14) and negative for the equations (15).

The integral $I = \int_0^\infty P' r \, P \, dr$ was calculated by Simpson's formula for P'_n and P'_{n+1}. For the equations that were actually calculated, the value $\left| \frac{I_{n+1} - I_n}{I_n} \right|$ was less than 0.5 %.

To estimate how the choice of the constant interval δ may have influenced the resulting value of I, I was calculated both for the constant interval δ and for the constant interval $\frac{\delta}{2}$. It was found that $\left| \frac{I_\delta - I_{\delta/2}}{I_\delta} \right|$ was less than 0.5 % in the actual cases.

Consequently the error in the values of α due to the numerical methods can be estimated to be less than 1 %.

ACKNOWLEDGEMENT

I would like to express my gratitude to Docent Inga Hjalmars for suggesting the subject, and for advice, encouragement and stimulating interest in the course of the work and also to Professor Oskar Klein for his kind interest. I am grateful to Professor M. Kotani for valuable discussions. Thanks are also due to Dr. P. Spiegelberg, who drew our attention to this problem. The present investigation has been financially supported by Statens Naturvetenskapliga Forskningsråd (The Swedish Natural Science Research Council).

Institute of Theoretical Physics, University of Stockholm, December 1957.

REFERENCES

1. For references, see STERNHEIMER, R. M., Phys. Rev. *96*, 951, 1954.
2. DRECHSLER, M., and MÜLLER, E. W., Z. Physik *132*, 195, 1952.
3. DRECHSLER, M., and HENKEL, E., Z. angew. Physik *6*, 341, 1954.
4. LIEPACK, H., and DRECHSLER, M., Naturwiss. *43*, 52, 1956.
5. BUCKINGHAM, R. A., Proc. Roy. Soc. A *160*, 94, 1937.
6. GUY, J., and HARRAND, M., Compt. rend. *234*, 616, 716, 1952.
7. POPLE, J. A., and SCHOFIELD, P., Phil. Mag. *2*, 591, 1957.
8. STERNHEIMER, R. M., Phys. Rev. *107*, 1565, 1957.
9. FISCHER-HJALMARS, I., and SUNDBOM, M., Acta Chem. Scand. *11*, 1068, 1957.
10. BETHE, H. A., and SALPETER, E. E., Handbuch der Physik, Bd. *35*, 330, 1957.
11. ALLEN, L. C., Ouarterly Progress Report, Oct. 15, 1955 Solid-State and Molecular Theory Group M. I. T., Cambridge, Massachusetts.
12. VAN VLECK, J. H., The Theory of Electric and Magnetic Susceptibilities, p. 154, 1932.
13. CONDON, E. U., and SHORTLEY, G. H., The Theory of Atomic Spectra, p. 53, 1953.
14. FOCK, V., and PETRASHEN, M. J., Phys. Z. Sovjet *8*, 457, 1935.
15. HARTREE, D. R., and HARTREE, W., Proc. Roy. Soc. A *164*, 167, 1938.
16. ABBOTT, J. A., and BOLTON, H. C., Proc. Roy. Soc. A *216*, 477, 1953.
17. RAHMAN, A., Physica *19*, 377, 1953.

Tryckt den 29 april 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB